THE FORMATION OF PLASMA BEAMS CONTAINING IONIC SPECIES

Stanley Singer, N. G. Kim, A. W. Merkl, L. B. Marantz
and C. Bodai

Research and Development Laboratories · RPI

Pasadena, California

The preparation of a plasma from substances stable under ordinary conditions can provide a steady state mixture of many reactive species. Neutral and ionic fragments are formed from the original reagent as a result of the high temperature and electron impact processes. The plasma involves a complex mixture of free radicals and ions in different levels of excitation. The formation of different species at different excitation levels in the plasma presents the possibility of different chemical reactions and products from a single reagent (c.f., for example, ref. 1). A study was made to devise a preparation of relatively pure reagents such as might be found in a plasma. A method in which the identity and excitation level of the reagent could be well known was desired. Ionic species have proven to be effective reagents, particularly in liquid phase organic reactions.

Many ionic species are readily formed by electron impact. The magnetron ion source is particularly suited for the formation of ions in large quantities with low energy electrons.[2,3] Specific methods have been required for large currents of particular ionic species. For example, a beam of protons has been prepared from hydrogen-saturated titanium by using an electrical discharge along the surface of the metal.[4] Ions have been made from the alkali metals by thermionic emission from a hot surface with a suitable work function such as tungsten.[5] The preparation of polyatomic ions has been carried out in ion sources similar to those used in mass spectrometers by electron impact. Electron energies most effective for ionization are used, usually from 70-100 electron volts. Such energies are much greater than the threshold required for ionization of most organic molecules and fragmentation results, providing a mixture of many different ions. The magnetron ion source provides a large current of ionizing electrons at low energies, and the resultant controlled ionization permits formation of plasmas containing selected ionic species.

---

1. K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, J. Am. Chem. Soc. 83, 2397 (1961).
2. B.G. Perovic, "Proceedings of the Third International Congress on Ionization Phenomena in Gases (Venice, June 1957)," Italian Society of Physics, Milan, October 1957, p. 813.
3. H.R. Kaufman, "An Ion Rocket with an Electron-Bombardment Ion Source, National Aeronautics and Space Administration, Technical Note D-585, Washington D.C., January, 1961.
4. K. W. Ehlers et al., Rev. Sci. Instr. 29, 614 (1958).
5. M. von Ardenne, "Tabellen der Elektronenphysik, Ionenphysik, und Ubermikroskopie," Deutscher Verlag der Wissenschaften, Berlin, 1956, Vol. I, p. 498.

EXPERIMENTAL

A dual-anode magnetron has been used for preparation of the ionic plasmas by electron impact. The usual magnetron configuration was modified, as shown in Fig. 1, by the addition of a central anode. A heated tungsten filament, used as the electron source, is placed between the two anodes also in a cylindrical surface. Electrons falling from this filament to the two anodes are provided with carefully controlled energies by placing the anodes at potentials only slightly above the appearance potential of the ion of interest. A magnetic field of approximately 500 gauss is applied along the axis of the source.

The outer cylinder of this source, which provides a plasma consisting largely of single ionic species and electrons, is a copper tube 7.5 cm. in diameter and 10 cm. in length as shown in Fig. I. An orifice 1.9 cm. in diameter in the cylinder allows the extraction and study of the ions. The gas to be subjected to electron impact is passed into the magnetron through a 3 mm. tube on the opposite side from this orifice. Copper cooling coils through which water circulates are wrapped around the outside of the cylinder. The central anode is a 1 cm. steel rod. The heated cathode is a tungsten filament 66 cm. in length and 0.76 mm. (0.030 inches) in diameter, and is drawn through insulated supports from one end to the other of the cylinder in alternating strands so as to be midway between the concentric anodes. The tungsten cathode was heated with approximately 30 amperes of 60 volt a.c. current.

In forming the desired plasma the ionizing gas is passed into the source at pressures of 5×10^{-4} to 1×10^{-3} Torr. If the electron energy required to ionize the gas is known, the anodes are placed a few volts above the necessary ionization potential, and the filament temperature is gradually increased until a collector placed a short distance outside the orifice indicates extraction of a strong current. Currents obtained with different anode potentials have been studied. If the ionization energy involved is unknown, the above procedure may be followed to determine effective conditions for generation of the desired plasma. Filament current, gas pressure, and anode potentials all affect ionization of a specific gas strongly, and these parameters interact strongly during operation of the magnetron. The ions formed were identified in this work by mass spectrometric analysis with a radio frequency quadrupole mass spectrometer.[6] The ionization of three gases was studied in this way, nitrogen dioxide (Matheson, 99.5%), tetrafluorohydrazine (Air Products and Chemical Co., Research Grade, 99+ %), and oxygen difluoride (General Chemical Div. of Allied Chemical Co.).

Extraction of the positive ion current when nitrogen dioxide was ionized in the magnetron with anode potentials of 12.5 volts showed that more than 99% of the ions formed were NO_2^+. Less than 1% of the ions in the extracted current were NO^+. With increasing anode potentials the amount of NO^+ increased. At 15 volts the beam contained approximately 5% of NO^+; and at 30 volts it contained 27% of NO^+. With tetrafluorohydrazine ionization at anode potentials of 12 volts gave a plasma containing largely NF_2^+, indicated by mass spectrometric analysis of the extracted ion beam in which 93% of the ions were NF_2^+. The remaining species were NF^+, and possibly a small quantity of NO^+ from impurities in the initial material. With increase in anode potentials the quantity of NF^+ in the extracted

6. W. Paul, H. P. Reinhard, and U. Von Zahn, Z. Phys. 152, 143 (1958).

current increased, similar to the effect observed with nitrogen dioxide. Ionization of oxygen difluoride was studied at anode potentials of 13 volts. The only positive ion detected was OF^+ which made up 76% of the ionic current extracted. Fluoride ion was also found; the negative ion was ca. 24% of the total extracted beam.

DISCUSSION

Magnetron Characteristics. - The concentric anode configuration of the magnetron used in these studies results in a markedly different electric field from that in the standard magnetrons. The strong axial magnetic field aids in efficient use of electrons for ionization, necessary in view of the low electric fields present. Ion currents on the order of 1 milliampere can be extracted from the magnetron by potentials of 1 to 10 volts, and if desired the flow of gas into the magnetron can be adjusted so that the extracted current corresponds to almost complete ionization of the entering gas. The anode potentials correspond to the maximum energy available from the ionizing electrons. With energies very close to the appearance potential of the desired ion the cross section for ionization is very low. This obstacle in forming a high concentration of ions is overcome in part by using a large electron current. Under typical operating conditions electron flow of 1 1/2 to 5 amperes to the anodes has been observed. Use of an oscilloscope to observe the currents flowing in the magnetron has shown that large 60-cycle electron pulses flow to the anodes. At typical pressures (0.5 - 1.5 microns) the pulse duration is 1-10 milliseconds; the pulse length increases with increasing pressure. These pulses briefly lower the anode potentials approximately 1/2 volt.

Formation of NO_2^+ Plasma. - Previous studies of the ionization of nitrogen dioxide by electron impact, aside from determinations of the ionization potential, showed that NO^+ was the predominant ion formed when electron energies of 40-70 volts were employed.[7,8] Although the possibility of forming a plasma containing almost 90% of NO^+ was shown,[7] NO_2^+ varied from less than 10% to perhaps 20% of the total ionic species, as estimated from the mass spectrometric peak intensities. Monatomic and diatomic positive ions of both nitrogen and oxygen were also present. Eight different ionization potentials varying from 9.78 electron volts up to 18.87 electron volts have been reported for nitrogen dioxide.[9-15] The higher ionization potentials reported have been attributed to formation of the ion in excited electronic states.

The use of lower energy electrons for ionization in this work evidently prevented formation of significant quantities of NO^+. Reduction of magnetron anode potentials

7. E. G. C. Stueckelberg, and H. D. Smyth, Phys. Rev. 36, 478 (1930).
8. R. A. Friedel, A. G. Sharkey, Jr., J. L. Schultz and C. R. Howard, Anal. Chem. 25, 1314 (1953).
9. T. Nakayama, M. Y. Kitamura, and K. Watanabe, J. Chem. Phys. 30, 1180 (1959).
10. D. C. Frost, D. Mak, and C. A. McDowell, Can. J. Chem. 40, 1064 (1962).
11. R. J. Kandel, J. Chem. Phys. 23, 84 (1955).
12. K. Watanabe, J. Chem. Phys. 26, 542 (1957).
13. W. C. Price and D. M. Simpson, Trans. Faraday Soc. 37, 106 (1941).
14. J. Collin and F. P. Lossing, J. Chem. Phys. 28, 900 (1958).
15. Y. Tanaka and A. S. Jursa, J. Chem. Phys. 36, 2493 (1962).

from 12.5 to 11.0 volts gave no further decrease in NO^+ concentration noted in ions extracted. The presence of some 6 reported ionization potentials lying between 9.78 and 12.3 electron volts, however, indicates that several electronic states may be present.

In previous investigations the formation of fragment ions was attributed, at least in part, to thermal dissociation as a result of the hot cathode.[7] The present results show that ionization in the magnetron occurs prior to dissociation and that higher electron energies can cause fragmentation.

Formation of NF_2^+ Plasma. - The use of tetrafluorohydrazine in preparation of the NF_2^+ plasma demonstrates how the ionizing gas can be selected to avoid the formation of undesired ions in certain cases. Ionization of ammonium trifluoride has been reported to give NF_2^+ as the major product.[16] The parent ion, NF_3^+ and the fragment NF^+ were also formed in significant quantities, however. If lower electron energies, slightly above the appearance potential of NF_2^+ from nitrogen trifluoride, were used it appears likely that significant, possibly greater, quantities of NF_3^+ would be formed because of the lower appearance potential of the latter ion and the rapid increase of ionization efficiency with electron energy near the appearance potential. In addition, fluorine atoms or possibly fluoride ions accompany the formation of NF_2^+ from nitrogen trifluoride. The symmetrical structure of tetrafluorohydrazine indicates the possibility of preparation of a plasma containing only NF_2^+ ions. The appearance potentials of ions from tetrafluorohydrazine have been determined, and mass spectroscopic studies have been made showing the ionic composition obtained by ionization with electrons of moderate energy.[17,18,19,20]

The formation of NF_2^+ with magnetron anode potentials of 12 volts, slightly below the published appearance potentials of this ion from tetrafluorohydrazine, 12.5 to 12.7 volts,[18,20] may indicate either the spread of electron energies in the magnetron or ionization of NF_2 radicals, which may form by dissociation of parent molecules and which have ionization potential below 12 volts.[20]

Preparation of OF^+ Plasma. - Mass spectrometric studies of the ionization of oxygen difluoride with 70 volt electrons showed the formation of the parent peak for OF_2^+ in greater quantities than OF^+.[21] The appearance potential of OF^+ from the neutral fragment OF was estimated at 13.0 electron volts, from the parent molecule, 15.8 volts. The magnetron anodes were therefore placed at 13 volts, below the appearance potential reported for OF_2^+, 13.7 volts. Extraction of ion current from the magnetron by means of external potentials and mass spectrometric analysis of the ions showed the presence of OF^+ and no other positive ions. The negative ion F^- was also observed, in quantities less than 1/3 the OF^+ current. Thus, attempts to ionize oxygen difluoride may provide a plasma containing large quantities of fluorine atoms in addition to the OF^+ and F^- ions.

ACKNOWLEDGMENT

The encouragement of Dr. J. F. Masi and the support of the Air Force Office of Scientific Research are gratefully acknowledged.

16. R. M. Reese, and V. H. Dibeler, J. Chem. Phys. 24, 1175 (1956).
17. C. B. Colburn and A. Kennedy, J. Am. Chem. Soc. 80, 5004 (1958).
18. J. T. Herron and V. H. Dibeler, J. Chem. Phys. 33, 1595 (1960).
19. C. B. Colburn and F. A. Johnson, J. Chem. Phys. 33, 1869 (1960).
20. A. Kennedy and C. B. Colburn, J. Chem. Phys. 35, 1892 (1961).
21. V. H. Dibeler, R. N. Reese and J. L. Franklin, J. Chem. Phys. 27, 1296 (1957).

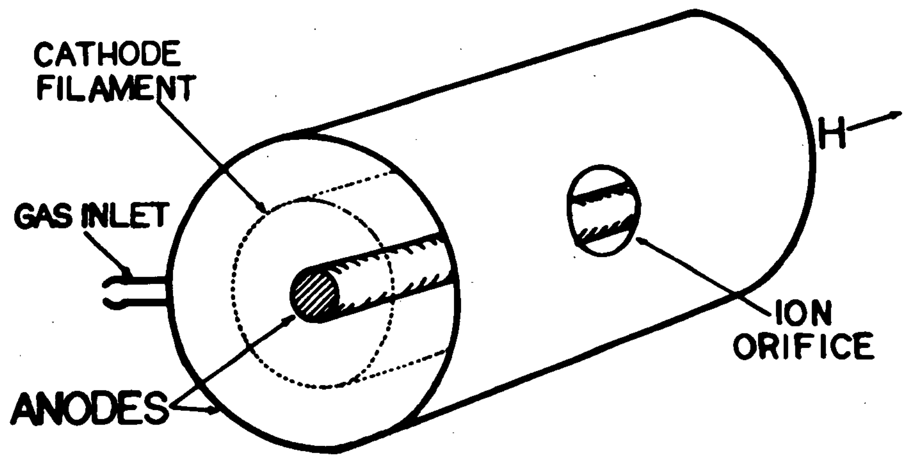

Fig. 1. Concentric Dual-Anode Magnetron